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Study of optical and electrical properties for ZrS_3 single crystals

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Abstract : Single crystals of the lamellar compound ZrS_3 has been grown by chemical vapour transport technique using iodine as a transporting agent. The grown crystals were characterized with the help of Energy dispersive analysis by X-rays (EDAX), which gives confirmation about the stoichiometry. Structural analysis has been carried out by X-ray diffraction (XRD). The optical band gap of as grown crystals has been obtained with the help of absorption spectra taken in the range of 300–1500 nm. An electrical resistivity measurement has been performed for this crystal in the temperature range of 303–550 K. The crystals were found to exhibit semiconducting nature in this range. The effect of pressure on electrical resistance of as grown crystals have been studied using Bridgman opposed anvil upto 8 GPa, which shows resistive behaviour of ZrS_3 single crystals. The results obtained are discussed in detail.

Keywords : ZrS_3 single crystal, EDAX, XRD, optical band gap, resistivity, Bridgman anvils

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1. Introduction

The zirconium trisulphide ZrS_3 is a member of transition metal trichaclogenide, which possesses chain like structure belonging to the crystal space group $P2_1/m$ [1]. The linear chain of metal atoms is parallel to the crystallographic *b*-axis, which is the growth axis. Six chalcogen atoms surround each metal atom forming distorted trigonal prisms. The crystal growth is in the form of layers which run parallel to the *b*-axis, and each chain in the layer are displaced from the neighboring chain by half of the unit cell along the *b*-axis. Resistivity, Hall coefficient and thermo electric power measurements of ZrS_3 single crystal along the chain axis have been carried out in the temperature range of 200–400 K [2].

The ZrS_3 exhibits a rather layer like semi conducting behavior [2–7]. In the anisotropic ZrS_xSe_{3-x} compounds the velocity of acoustic wave propagating in a direction parallel to the fibers decreases linearly as the selenium content is progressively increased [8]. An indirect band gap of 2 eV for ZrS_3 single crystals was measured [9]. The specific heat of the semiconducting compounds $ZrSe_3$ and ZrS_3 have been measured in the temperature range of 8–200 K [10].

ZrS_xSe_{3-x} exhibit continuous regions of solid solubility. Diffuse reflectance measurements show that $ZrS_{3-x}Se_x$ exhibit semiconduction [11]. Raman scattering for ZrS_3 was reported as a function of hydrostatic pressure [12]. Thermoreflectance spectra of $ZrS_{3-x}Se_x$ single crystals have been measured at 50 K. The thermoreflectance spectra of ZrS_3 and $ZrSe_3$ are discussed through direct and indirect exciton transition [13]. The first-order Raman spectra of one-dimensional semiconducting compounds ZrS_3 at 300 and 77 K. Four phonons have been detected and associated with the crystal's symmetry [14]. The resistive nature of ZrS_3 is inferred from the resistance *versus* pressure measurements. The resistivity increases with the increase in pressure [15]. A detailed study of the valence band by synchrotron radiation photoemission spectroscopy had demonstrated the existence of paired-anion ligands in zirconium trichalcogenides [16].

In this paper, we report the growth of ZrS_3 single crystals using chemical (iodine) vapour transport technique. Energy dispersive analysis by X-rays (EDAX) give

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confirmation about the stoichiometry of the grown crystals and X-ray diffraction (XRD) studies give information about the structural properties. Optical band gap has been carried out using absorption spectra taken in the range of 300–1500 nm. Resistivity has been measured as a function of temperature in the range of 303–550 K. The effect of pressure on resistance of these crystals was studied using Bridgman opposed anvil setup upto 8 GPa.

2. Experimental

The reddish-needle shaped, layered single crystals of ZrS_3 have been grown by the chemical vapour transport (CVT) technique using iodine as a transporting agent. Pure elements zirconium foil (99.99%), sulphur (99.97%) and selenium (99.98%) in stoichiometric proportions were filed in the quartz ampoule along with iodine (2 mg/cc). This ampoule was sealed at 10^{-5} torr pressure. Then the ampoule was rigorously shaken to ensure the proper mixing of the constituent elements and placed co-axially in the two-zone furnace with appropriate temperature gradient for crystal growth. The optimum conditions for growth of ZrS_3 single crystals are given in Table 1.

Table 1. Growth parameter of ZrS_3 single crystal grown using chemical vapour transport technique.

Ampoule dimension		Temperature distribution		Physical characteristics of crystals			
Length mm	ID mm	Hot zone K	Cold zone K	Growth time hr	Plate area mm^2	Thickness mm	Colour
250	22	1173	1123	370	45	0.09	Red shining

The Energy Dispersive Analysis of X-ray (EDAX) has been carried for confirmation of stoichiometry of the grown crystals. X-ray diffraction (XRD) study has been performed for the structural characterization. The X-ray diffractograms were obtained with Philips X-ray diffractometer PW1820 employing CuK_α radiation. The absorption spectra were obtained by means of a UV-VIS-NIR DK 2A spectrophotometer in the range of 300 nm to 1500 nm. All measurements were taken at room temperature with the incident beam normal to the basal plane *i.e.* along the *c*-axis of the as grown flakes.

The high temperature resistivity measurement parallel to c-axis *i.e.* normal to the basal plane was carried out in the temperature range of 300–550 K for this crystals. In order to achieve higher pressures, Bridgman suggested the use of two opposed anvils. In the basic design of the anvils, the truncated anvils of tungsten carbide are supported by steel binding rings with interference fit to apply inward acting radial stresses.

This design uses Bridgman's principle of 'massive support.' Bridgman anvil can be readily used upto 10 GPa. The sample is in the form of a thin disk surrounded by a gasket, normally of pyrophyllite material with talc powder as pressure transmitting medium. A four-probe method was used to evaluate the resistance of the ZrS_3 crystals.

3. Results and discussion

The lattice parameters for as grown crystals are found to be a = 5.12 Å, b = 3.62 Å and c = 9.02 Å from XRD analysis. The interpretation of experimental results, viz. the dependence of absorption coefficient 'α' in the terms of the direct and indirect transitions, is most often performed with the help of formula derived for three dimensional (3D) crystal. Their simplest form is as follow [17] :

$$\alpha h\nu = A(h\nu - E_g)^r, \quad \text{for direct band gap;} \quad (1)$$

$$\alpha h\nu = \sum_j B_j (h\nu - E_g' \pm E_{pj})^r, \quad \text{for indirect band gap.} \quad (2)$$

Here, α is the absorption coefficient, calculated as a function of photon energy from absorption *vs.* wavelength curve. $h\nu$ is the energy of the incident photon, E_g the energy for the direct transition, E_g', the energy for the indirect transition and E_{pj}, the energy of the phonons assisting at indirect transition. A and B are parameters depending in the more complicated way on temperature, photon energy and phonon energies E_p.

From the graph of $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$ and $(\alpha h\nu)^2$ *vs* $h\nu$ as shown in Figures 1 and 2, it is possible to determine the indirect as well as direct band gap respectively, for ZrS_3 single crystals. These curves indicate discontinuous straight lines. It is quite possible that they represent indirect interband transition involving the emission or absorption of photons. The band gap obtained by

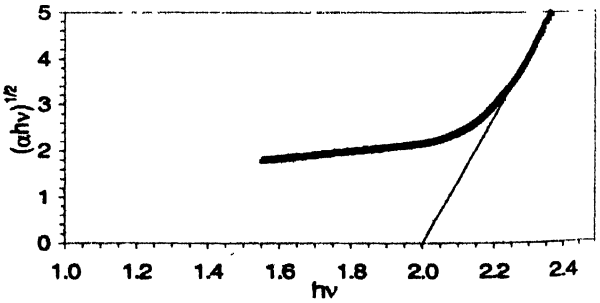

Figure 1. The graph of $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$.

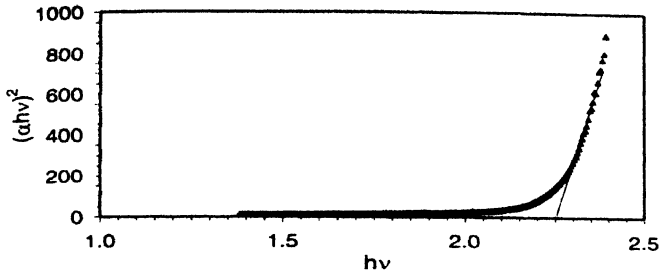

Figure 2. The graph of $(\alpha h\nu)^2$ *vs.* photon energy $h\nu$.

extrapolating the linear part to zero. The indirect as well as direct band gap is found to be 2 eV, and 2.28 eV respectively. The graph of $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ *vs* $h\nu$ has been shown in Figure 3.

It can be clearly seen from the Figure 3 that the derivatives are step function of energy with four steps well defined in the ranges $E_1 < E < E_2$, $E_2 < E < E_3$, $E_3 < E < E_4$ and $E_4 < E$. Indirect band gap is given by $E'_g = \dfrac{E_1 + E_4}{2} = \dfrac{E_3 + E_2}{2}$ and the phonon energies are given by $Ep_1 = \dfrac{E_4 - E_1}{2}$ and $Ep_2 = \dfrac{E_3 - E_2}{2}$.

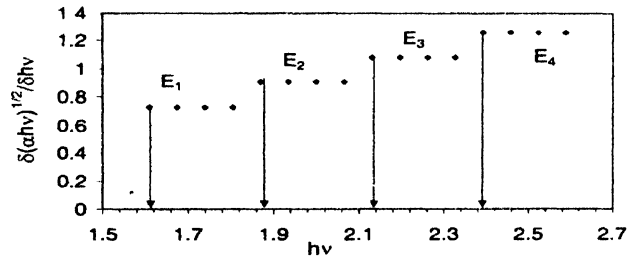

Figure 3. The graph of $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ *vs.* $h\nu$.

The values of indirect band gap, direct band gap and phonon energy thus obtained are presented in Table 2.

Table 2. The values of band gap and phonon energies for ZrS_3.

Parameter	Value of ZrS_3 3-dimension
E_1 (eV)	1.609
E_2 (eV)	1.870
E_3 (eV)	2.131
E_4 (eV)	2.392
E'_g (C)(eV)	2.005
E'_g (E) (eV)	2.000
Ep_1	0.391
Ep_2	0.130
E_g (eV) (Direct)	2.280

The graph of log $\rho_{\|\|}$ *vs* 1000/T in Figure 4, shows that the resistivity decreases with the increasing temperature. The electrical dc resistivity is a function of pressures. As shown in Figure 5, the resistivity increases with the increase in pressure, which shows resistive behaviour of the grown crystal upto 8 GPa. This result is completely opposite to those obtained with respect to temperature.

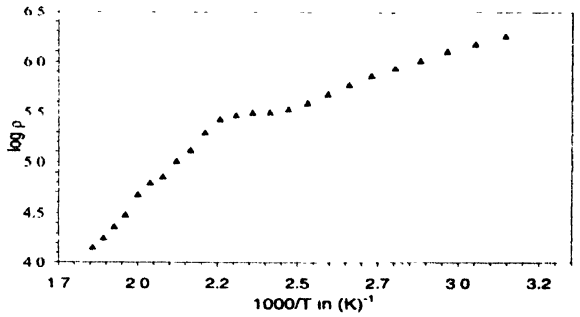

Figure 4. The graph of log ρ *vs.* 1000/T.

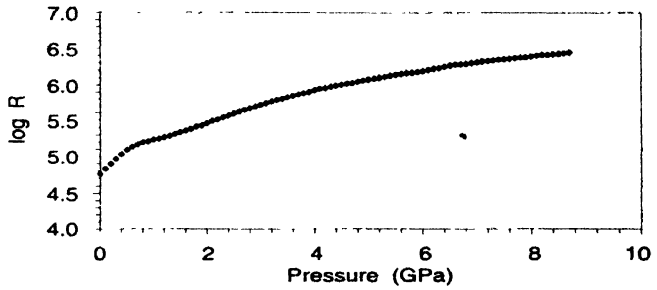

Figure 5. The graph of log R *vs.* pressure in GPa.

4. Conclusions

(i) The chemical (iodine) vapour transport (CVT) technique is most suitable for the growth of large size, needle shaped-reddish single crystals of ZrS_3. The optimum condition for the growth is given.

(ii) The indirect and direct band gap is 2 eV and 2.28 eV. respectively for ZrS_3 single crystals.

(iii) The resistance increases with pressure upto 8 GPa for ZrS_3 single crystals. A possible explanation for the increase in resistance might be attributed to the detachment of sulphur atom from the unit cell with increasing pressure.

(iv) ZrS_3 has semiconducting behaviour in the temperature range of 300–550 K.

(v) From the XRD data, we conclude that the ZrS_3 has monoclinic structure.

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